Fuel 222 (2018) 617–626

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Effects of different extracted components from petroleum pitch on mesophase development

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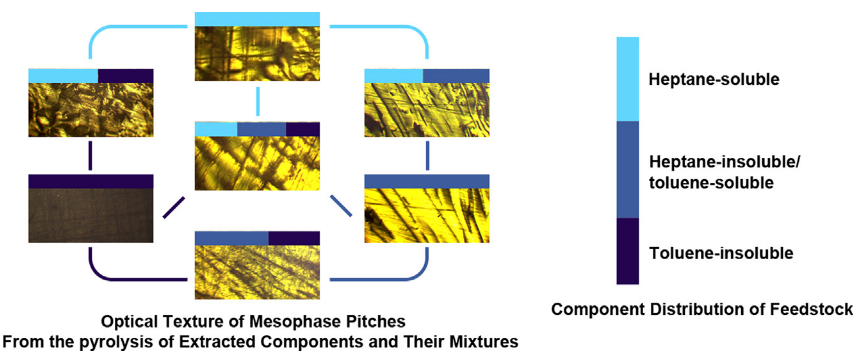
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Extracted component
Mesophase pitch
Interactive effect
Alkyl chain
Naphthenic structure

ABSTRACT

Naphthenic-based petroleum pitch was divided into three components, including heptane-soluble (HS), heptane-insoluble/toluene-soluble (HITS) and toluene-insoluble (TI), by sequential extraction with heptane and toluene. Mesophase pitches were prepared by direct condensation of the extracted components and their mixtures. Effects of different components on formation and development of mesophase structures were investigated. Results showed that HITS was the optimal component for preparation of mesophase pitch with large domain structure, low softening point, high carbon residue and ordered microcrystal structure. Interactive effect indexes were cited to monitor the interaction of these components on mesophase development. The component HS with rich alkyl chains accelerated the carbonization via chain breaking at the initial stage of reaction, and HITS with abundant naphthenic structures alleviated the carbonization through hydrogen-transfer reaction during the aggregation process of aromatic molecules, and TI as initial nucleus could trigger the generation of mesophase spheres. However, the mixture of HS and TI possessed a weaker interactive effect on mesophase development compared to the other two mixtures. This was mainly due to the differences in molecular weight distribution and molecular structure between HS and TI. Furthermore, naphthenic structures had a better improving effect than alkyl chains on the generation of high-quality mesophase pitches.

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https://doi.org/10.1016/j.fuel.2018.03.011
Received 25 November 2017; Received in revised form 1 March 2018; Accepted 4 March 2018
Available online 23 March 2018

1. Introduction

Mesophase pitch is widely recognized as excellent precursor for making high quality carbon materials [1]. Mesophase pitch based carbon material has great exploitation potentiality and broad application prospects in the field of new carbon materials due to its low price, high strength, good electric performance, and environmental protection, etc [2,3]. Naphthenic-based petroleum pitch with abundant aromatic fractions has been extensively used to produce high-quality mesophase pitch [4,5]. Therefore, the research on preparation and formation of petroleum pitch based mesophase pitch are the hotspot and focus in the field of carbon materials.

As previously reported, the influences of structural composition [6–8] and molecular structure [9–11] of pitches on optical textures and rheological properties of mesophase pitches have been studied widely. Menéndez et al. have discussed the relationships between compositions of pitches and optical textures of cokes [8]. The structural composition of pitches is proved to be the determining factor for the improvement of products' optical textures. Miyake et al. have tried to monitor the effects of alkyl structures on the development of anisotropic structures [11]. They have found that the optical texture and anisotropic contents varied depending on the number and steric size of alkyl groups in mesophase precursors. After studying the formation of mesophase pitches prepared by naphthalene and methylnaphthalene, Mochida et al. suggested that the alkyl structures worked efficiently for improving the liquid-crystal structures of mesophase [12–14]. Korai and Yoon also proposed that the alkyl chains in mesophase precursors have important effects on the properties of mesophase pitch [15,16].

Additionally, a series of studies on pyrolysis of parent pitch and pitch component with different properties have shown that the molecular-weight distribution of pitch component was mainly responsible for the changes in optical texture and microcrystal structure of mesophase pitch [17–20]. Torregrosa-Rodríguez et al. has investigated the roles of parent pitches and their fractions with different molecular-weight distribution played on the solubility and optical textures of resultant cokes [19]. They note that the pitch with narrow molecular-weight distribution is easy to generate a mesophase with good rheological property and large domain structure. Sparvoli et al. have also emphasized the significant influence of molecular-weight distribution in petroleum pitch on the mesophase development [20].

Research on the components of feedstock is an effective way to study the influences of structural composition of feedstock on the mesophase development [21]. Liu et al. [22] have evaluated the relative hydrogen-donating abilities of different heavy oils and their fractions during mild thermal conversion. Moreover, the interactive effects of fractions on the coke formation were investigated. Wang [23] also studied the interaction of the extracted components from residue oil during the thermal reaction. They defined an interactive effect index by measuring the hydrogen transfer abilities of fractions to explain the carbonization behavior. Furthermore, after investigating the carbonization behaviors of residue and its extracted fraction during the preparation of mesophase pitches, Yang [24] found that the heavy components in the feedstock led to the formation of initial coke, while the light components play a role in in inhibiting coke formation. Alvarez [25] and Machnikowski [26] et al. also suggested that the fractions of atmospheric residue and coal-tar pitch showed different reaction activities, and they could interact with each other during the thermal reaction.

These studies have reduced the chemical complexity of pitch and confirmed the important influences of structural composition and molecular-weight distribution of feedstock on the properties of carbonized products. However, the pyrolysis behavior of pitch components should be traced by more effective analyses, and the exact roles of components playing in mesophase development still need to be studied further. This paper was concerned with the influences of structural composition of three pitch components extracted from a naphthenic-based petroleum pitch on the optical textures, softening points, carbon residues, molecular and crystal structures of carbonized products. Moreover, the interactive effects of the extracted components on the formation and development of anisotropic structures were discussed.

Table 1
Basic properties of feedstock and its components.

Sample	M	Elemental composition/wt%					n(H)/n (C)	Yield[a]/wt%
		H	C	S	N	O		
F	489.12	8.71	91.14	0.08	0.05	0.02	1.15	–
HS	416.91	9.78	90.01	0.09	0.07	0.05	1.30	34
HITS	472.53	8.86	91.02	0.07	0.03	0.02	1.17	39
TI	596.95	7.08	92.77	0.08	0.05	0.02	0.92	27

[a] Mass percentage of the component (HS, HITS or TS) in the feedstock F.

2. Experimental section

2.1. Materials

A naphthenic-based petroleum pitch (named F) from CNOOC Company was divided into three components: heptane-soluble (HS), heptane-insoluble/toluene-soluble (HITS) and toluene-insoluble (TI) by sequential extraction with heptane and toluene according to ASTM D6560-2000(2005). Table 1 listed the basic properties of feedstock and its three extracted components. The mass percentage of HITS (39%) in the feedstock F was a little higher compared to that of HS (34%) and TS (27%). The average molecular weight (M) of components increased in the order of HS < HITS < TI, while the change tendency of H/C atomic ratios of the three components was opposite to that of relative molecular weights. Moreover, the feedstock F and its three components all contained little sulphur, nitrogen and oxygen.

2.2. Thermal treatment

The three mixtures of HS and HITS, HS and TI, HITS and TI, in proportions to the percentages of components in the petroleum pitch F, were respectively named as A, B and C. The F and its extracted components HS, HITS, TI, A, B and C were thermally treated at 450 °C under constant pressure of 4 MPa. The resultant products, obtained at reaction time of 4.5 h, were named HS-MP, HITS-MP, TI-MP, A-MP, B-MP and C-MP.

2.3. Characterization

2.3.1. Elemental composition analysis

The contents of elements (H, C, S and N) in the feedstock were determined by a PE-2400 Series HCSN elemental analyzer; while the content of oxygen was obtained by difference method.

2.3.2. Average molecular weight analysis

The average molecular weights of F, HS, HITS and TI are characterized by gel permeation chromatography (GPC) using a Waters 2695 GPC chromatograph with a refractive index detector and two Polymer Laboratory Gel columns (100 and 500 Å). Toluene was used as the mobile phase [27,28].

2.3.3. Fourier transform infrared (FTIR) spectroscopy

The functional groups of feedstock and mesophase pitch were characterized by a Nicolet S-215 FTIR spectrometer. The spectra were an average of 32 scans with a resolution of 4 cm^{-1} in the region of 4000–500 cm^{-1}. The aromatic degrees (fa) of extracted components were calculated according to the formula fa = 0.574Abs1600/ (Abs1600 + 0.16 Abs1460 + 0.23Abs1330) + 0.024, and the molar ratios of $-CH_2-$ to $-CH_3$ (r) were calculated by the formula